ACE-7

HOW FIRES START AND HOW THEY BURN

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Washington, D. C.

Pennsylvania Firemen's Training Conference
State College, Pa.
August 28, 1939.

CHEMISTRY OF FIRE

The reason why a material ignites and burns has often been referred to as "the chemistry of fire." We do not, however, have to know much of chemistry to understand combustion. We see it every day, in many forms, and we have a sufficient knowledge of the general cause and behavior of fire to be able to understand what takes place without any technical detail of the occurrence known as ignition and burning.

The simple definition of a combustible is "anything which will ignite and burn." For a fireman, however, there is need of a more definite idea, not as to what is a combustible, but as to:

(1) Why is a thing combustible?
(2) What takes place when substances ignite and burn?
(3) Means of preventing combustion, or stopping it when it has started.

SOME PRINCIPLES OF COMBUSTION

In considering some principles of combustion it will be helpful to define some of the common terms encountered by firemen, such as:

(1) Combustion
(2) Combustible
(3) Supporter of Combustion
(4) Heat of Combustion
(5) Slow Combustion
(6) Oxidation
(7) Ignition Temperature
(8) Flash Point
(9) Spontaneous Ignition

Combustion in the wide sense of the term is a chemical reaction attended with light and heat, except perhaps in the initial stages. It is commonly restricted, however, to the direct union of a substance with oxygen. Two substances at least are concerned in every combustion:

(1) The "combustible," or the body which burns;
(2) The "supporter of combustion," or the gas in which the combustion takes place.

There are, however, some other chemical reactions not involving oxygen which also are known as "combustion" or "fire," - as for example, the reaction between

(1) Chlorine and hydrogen,
(2) Chlorine and ammonia,

both of which are attended by the evolution of heat and light.
"Heat of Combustion." While the heat evolved by the "oxidation" or combustion of a given substance is the same regardless of whether the reaction is slow or rapid, the temperature developed depends largely on at least

three important factors:

(1) The speed of the reaction
(2) The physical condition of the combustible
(3) The surroundings.

"Slow Combustion." Some substances under certain conditions react slowly, the heat developed being dissipated as fast as liberated, and consequently no rise in temperature occurs. As distinguished from combustion proper, slow combustion is a process of oxidation which is not attended by the development of light and heat.

"Oxidation." This may be defined as the union of a combustible substance with oxygen. This union may be accompanied by light and heat, as in "combustion," or it may be "slow combustion." The rusting of iron is an example of what we ordinarily call slow combustion or slow oxidation. On the other hand, finely-divided iron may oxidize rapidly enough to ignite.

"Ignition Temperature." It is a matter of common knowledge that combustibles all about us remain for years in the presence of a supporter of combustion without taking fire. Fortunately there is little, if any, chemical reaction between most combustibles and the oxygen of the air at ordinary temperatures. If the combustible, however, is heated sufficiently, reaction with the oxygen of the air may be followed by ignition. In other words the temperature of the combustible may reach a point at which the reaction becomes self-sustaining. This temperature level, which is necessary to start combustion, is known as the "ignition point," or "ignition temperature."

The "ignition temperature" is therefore the temperature required to start actual combustion. This ignition temperature depends on a number of factors, but when determined under test conditions comparable with those met with in practice, is of the highest practical importance to the fire service.

"Flash Point." The flash point of a liquid is the temperature at which it gives off vapors sufficient to form an ignitable mixture with the air contained in the vessel used.

"Spontaneous Ignition." The source of heat causing ignition may be a flame, spark, radiation, a hot surface, friction, or chemical reaction. When the primary source of heat is chemical action (1) due to the combustible itself, or (2) between the combustible and the supporter of combustion, the process is known as "spontaneous heating," and if the ignition temperature is reached it is "spontaneous ignition."

The primary reactions causing spontaneous ignition may be preceded by other sources of heat such as microbial action, - as in the fermentation of hay.

MOST COMBUSTIBLE MATERIALS LARGELY COMPOSED OF CARBON

It can be briefly stated that most materials found in ordinary use - such as wood, paper, cloth, vegetable matter, and oils - are largely composed of carbon. Charcoal and coke, for instance, are almost pure carbon and it is known to every one that all these materials can be reduced to some form of carbon.

Just what takes place in the burning of a material is a chemical combination of the oxygen in the air with the carbon in the material. There may be other elements in the material which also combine with the oxygen. For instance, ordinary commercial or natural gas will contain hydrogen, and in many materials will be found sulphur, as well as numerous lesser known elements, all of which will combine with oxygen. Even the metals in ordinary use combine to a greater or less degree. When in a very finely divided state such as aluminum powder, this combination with oxygen can be extremely rapid, with explosive violence.

FACTORS INFLUENCING COMBUSTION

There are at least four principal factors which influence combustion or burning:

(1) Presence of oxygen
(2) Heat
(3) Form of the material
(4) Progressive action

(1) Presence of Oxygen

Oxygen normally composes about 21 per cent of the air, and under these conditions burning can take place very readily if other favorable conditions exist. When the percentage of air is reduced, combustion is also lessened. This reduction of oxygen can take place in several ways:

(a) Other gases may be liberated and become mixed with the air, resulting in a dilution of the oxygen down to less than 15% - at which point most materials will stop burning.

(b) There may be an actual exclusion of air. Everyone has seen the effect on a bonfire when wet leaves are thrown on it, or when sand is poured on burning material. This acts as a cover or blanket and prevents air from reaching the material.

(2) Heat

The second factor affecting combustion is heat. Practically all articles and materials in common use must be heated before this combination with the oxygen of the air will take place and application of heat has to be continued to keep it burning. If the heat is not carried from the burning part of the material to the unburned part, the fire will go out.

Example: This is best illustrated with a match which will continue to burn if held with the flaming end down so that the flame heats up the unburned part, but may go out if held with the burning end upward.

Ignition Temperature Varies with Materials

The temperature at which this oxidizing action, with the evolution of flame, starts - varies with different materials. As an example: Wood normally requires a temperature of about 500° to 750° F. before it begins to burn. On the other hand, if wood is exposed to a temperature of about 400° F. for a period of approximately half an hour, it will ignite.

This lowered temperature of ignition where wood has been exposed to heat for a considerable period of time has a marked influence on fire fighting. It explains, for instance, why intensity of fire increases so rapidly after the first ten to thirty minutes and accounts for buildings bursting into flames throughout the interior where there has been a delay in the discovery of the fire.

Under these conditions, where a fire in a closed building has been smoldering for a considerable time, it is probable that all the woodwork and other burnable material has reached the ignition point. Then all that is needed is sufficient oxygen, which it will receive when a window is broken, a hole burned through the roof or a door opened.

It must be remembered in connection with this, that it is not necessary for a flame or spark to be applied for the material to ignite at these temperatures. All that has to happen is for sufficient air to be present, and ignition will take place. It is this form of ignition which produces "back draft," when firemen open up a building and thus add oxygen to gases which are heated above their ignition temperature.

(3) Form of Material

The third factor in considering combustion is the form of the material or its physical condition.

It is common knowledge that the finer or thinner a material is, the easier it is to ignite it. For example - shavings, chips and excelsior quickly ignite and burn rapidly. This material when baled or in bulky form, or the larger timbers in a building, char on the outside - but actual combustion of the entire mass is slow. This is a vital matter in the study of fire fighting. It explains why heavy timber, or in so-called mill construction, buildings are safer to fight fires in than the ordinary joisted or frame building.

Some of the most common combustibles are the oils, greases and fats. These are first turned into gas or vapor, then with proper mixture of air there can be combustion. Some of the oils, as gasoline, will vaporize at ordinary temperatures, and therefore where they are present, and the vapors can mix with the air, there is always great danger of fire. However, so

long as the material can be kept in liquid or solid form, or can be kept in a container, such as a tank, drum or can, or in pipe lines, there is practically no danger of ignition or fire.

(4) Progressive Action

The fourth factor in regard to combustion is that it is progressive action.

Example: When wood burns the first or initial action is not complete combustion. The carbon and oxygen continue to form carbon monoxide which is in itself a combustible gas, which when given enough air, will burn. Carbon monoxide corresponds closely to illuminating gas, and will not ignite until a temperature of about 1100° F. is attained.

In many fires this action of forming carbon monoxide and then burning to carbon dioxide, or the gases of complete combustion, takes place right at the burning material, and gives visible flame seemingly coming direct from the log, or beams, or other form in which the combustible material may be.

HAZARDS FROM CARBON MONOXIDE

When there is not enough heat, or when there is an insufficiency of air, carbon monoxide will be given off in large quantities, and being of about the same weight as air, will diffuse or spread. Being heated it will tend to rise to the upper parts of the building.

Burning oil and grease are prolific producers of carbon monoxide, in part because the original ignition temperature is low, about 500 degrees, and therefore much below the 1100 degrees necessary to burn it to carbon dioxide, and in part because air cannot get to the central part of the flat surfact of the material.

This partial burning of the gases liberated through the heating of combustible material plays a very important part in the scheme of fire fighting. Not only are the gases combustible, and therefore of an explosive nature, but they are dangerous to life and because of small particles of unburned carbon or soot, they impede the firemen in locating and extinguishing the fire.

CLASSIFICATION OF SUBSTANCES SUBJECT TO SPONTANEOUS HEATING OR IGNITION

No sharply defined or scientific classification of substances subject to spontaneous heating has been worked out, but for convenience those substances which have been found to cause or undergo spontaneous ignition may be divided into four groups as follows:

Group 1 - Noncombustible substances which may cause ignition - lime.

Group 2 - Substances of low ignition temperature.

Group 3 - Oils, fats, metals (finely divided), charcoal and coal.

Group 4 - Agricultural products - hay and grain.

Group 1 - Noncombustible Substances

This group is mentioned first because it represents spontaneous heating in its simplest aspect. Calcium oxide (unslaked lime) is the outstanding member of this group. Many fires caused by wetting of lime in the presence of combustibles are on record. It is of interest to note that the reaction of one pound of lime with water evolves 124,000 calories (493 B.T.U.). Included in this group are barium oxide, sodium peroxide, and other chemicals which in contact with water may evolve sufficient heat to cause ignition of common combustibles.

Example: Investigation of a fire of unknown origin indicated that barium oxide was the source of ignition. It appeared that when a wooden keg containing the barium oxide was opened, enough moisture was present to cause a reaction, which resulted in ignition of surrounding combustibles.

Application: It is evident that, as a measure of safety, chemicals of this group should be kept away from combustibles.

Group 2 - Substances of Low Ignition Temperature

A well known member of this second group is often called "spontaneously inflammable phosphine," which, however, is not pure phosphine. It is stated in the literature that the pure gas does not ignite below 212° F. but is highly flammable and is easily ignited in contact with air. It appears that the spontaneous ignition of phosphine at ordinary ambient temperatures is due to the presence of the vapor of the liquid hydride of phosphorus which is very likely to be produced in reactions yielding phosphine.

Examples:

(1) It has been claimed that the hydride of phosphorus may be produced by the putrefaction of damp sawdust, resulting in ignition, but available data on this are meager.

(2) Silicon hydride as ordinarily prepared is also spontaneously flammable in air at ordinary temperatures. It is stated in the literature that the pure gas does not take fire at ordinary temperatures, but ignites if slightly warmed. The hydrides of silicon and phosphorus are met with in chemical laboratories, but are not likely to be encountered elsewhere.

(3) The reactions of sodium and potassium with water, which are decomposed with the evolution of hydrogen, are of more practical interest. In the case of potassium, the evolved hydrogen is ignited in the presence of air by the heat of the reaction even at ordinary ambient temperatures. The reaction of sodium with water is less violent than that of potassium and ignition of the evolved hydrogen does not occur as readily.

(4) The combustion of cellulose compounds such as paper may be extinguished by chlorine, but turpentine, ammonia, and a number of others ignite spontaneously in an atmosphere of chlorine even at ordinary ambient temperatures.

Group 3 - Oils

The best known members of the third group are linseed, soybean and olive oils, which, in the presence of air at ordinary room temperatures, undergo oxidation with the evolution of heat. Although their ignition temperatures are comparatively high, the heat generated by the oxidation is sufficient to cause ignition under favorable conditions.

The reaction is promoted by exposure of a relatively large surface area of the oil to the oxygen of the air. This is readily accomplished by the impregnation of a fibrous material such as cotton with oil.

The form in which the oily fibrous material is exposed to the air also influences the reaction, and affects the rate of dissipation of heat. If the oily mass is compact, the oxygen supply from the atmosphere is necessarily restricted and if exposed to air currents, the heat loss may prevent a rise in temperature.

Group 4 - Agricultural Products

There is a wide divergence of opinion as to the underlying causes of the spontaneous ignition of hay and other agricultural products. There are theories that ignition is caused by:

(1) Bacterial heat
(2) Enzymes causing oxidation (oxidases)
(3) Pyrophoric carbon
(4) Pyrophoric iron

The subject is complex and further experimental data are needed.

From the research work in the U. S. Department of Agriculture it appears that the spontaneous ignition of these products is a process of two or more stages. The first stage of the spontaneous heating (up to about 70° or 80° C. or 158° to 176° F.) is caused primarily by fermentation or other microbiological action, it being well known that such processes generate heat. When the temperature, however, exceeds about 176° F., the activity of micro-organisms and enzymes is supposed to cease. The rise of temperature in later stages of the process is considered to be due to chemical oxidation. It is thought that unsaturated and inter-

mediate products may be formed in the first or microbial stage, the subsequent oxidation of which is a factor in causing ignition. Some of the other results of this work in the Department of Agriculture can be summarized as follows:

(1) The spontaneous ignition of hay is most likely to occur from 2 to 6 weeks after storage.

(2) As a safety measure the moisture content should not exceed about 30 per cent by weight of the hay.

(3) Hay should be cured before being placed in storage.

(4) Mows should not exceed about 10 tons.

(5) The division of large mows into small compartments by means of alleyways or open-work partitions would facilitate drying and aid in dissipation of heat.

(6) Salt (sodium chloride) may retard fermentation, but the evidence available indicates that salting of hay cannot be relied upon to prevent its spontaneous ignition.

(7) Losses would be greatly reduced if hay was stored in isolated structures separated a safe distance from farm buildings.

Much remains to be learned about spontaneous ignition and further research may be expected to yield valuable data as a basis for more effective methods of preventing large losses from this cause.

TWO WAYS OF PREFENTING OR STOPPING COMBUSTION

Combustion can be prevented or stopped in either one or both of two ways.

(1) By keeping the temperature of the material below the ignition temperature.

(2) By excluding or diluting the air so that sufficient oxygen is not available for ignition.

The application of water in an intelligent manner, which tends to accomplish both of these objectives, has proved to be the best method of preventing destruction of combustible materials.

Some of these materials may, however, be found in such form, shape or extent as to make some special fire extinguishing medium particularly well suited.

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